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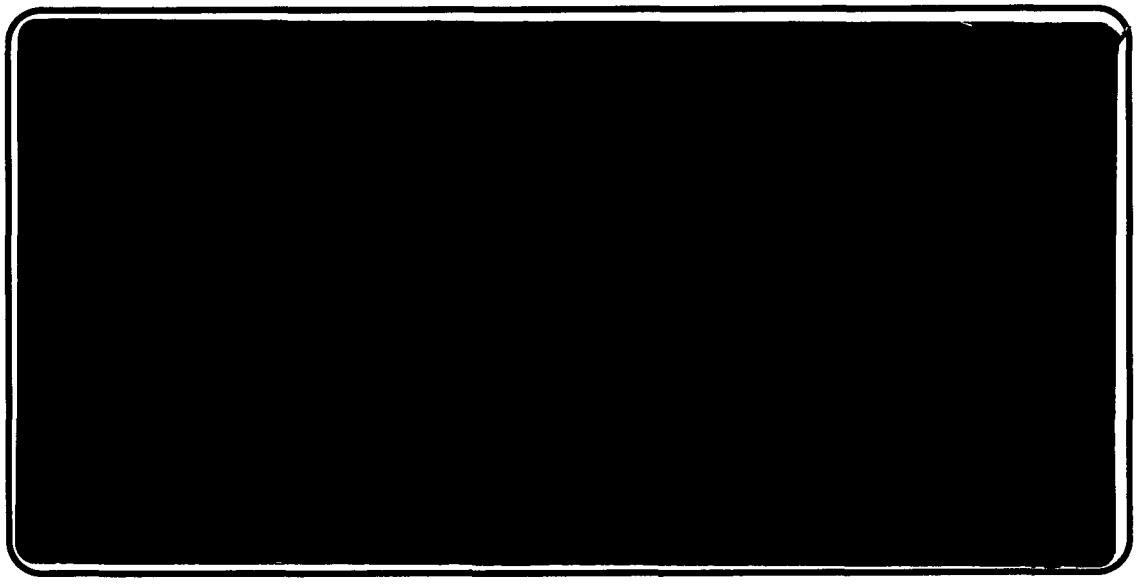

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DEPENDENCE OF FIBER/FIBER BONDING ON SOME PAPERMAKING VARIABLES

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ABSTRACT

The bond breaking load and bonded area of individual fiber/fiber bonds were measured using a new fiber load elongation recorder (FLER2) and Page's polarized light scattering technique, respectively. Lightly (570 mL CSF) and moderately (345 mL CSF) refined fibers with fines subsequently removed produced bonds of equal strength. Bonds between latewood fibers were substantially stronger than those between earlywood fibers. Polymeric strength aids interacting with the fibers by either covalent or ionic bonding increased the bond strength by a factor of two.

INTRODUCTION

The strength of a sheet of paper with randomly oriented fibers has been shown both theoretically [1,2] and experimentally [3] to depend on two factors. These are 1) the strength of the individual fibers and 2) the strength and number of the bonds between them. Page, et al [4] have reviewed the earlier work on the strength of

single fibers and have also shown that the strength isprimarily dependent upon the fibril angle in the S2 layer and on fiber defects. Using larger fiber populations Hardacker and Brezinski [5] showed that fiber strengths of a given pulp had approximately log-normal distributions with large coefficients of variation. They suggested that it may be necessary to include information about the distribution of fiber strength as well as its average value in correlations with sheet strength.

The bond shear strength of individual fiber bonds has been measured by a number of workers [6-15]. They have investigated the effects of springwood vs. summerwood [7,8,10,15], refining [6,12], and yield [7,10-12] sometimes with contradictory conclusions. Bonds were formed either between two fibers [6-10,15], between a fiber and a shive of the same material [7,14], or between a fiber and a cellophane strip [10-13]. Sensitive instruments were constructed to measure the maximum load at failure. Bond areas were assumed to be either the total area of fiber overlap [8,10-15] or the area in optical contact [6,7,9] as determined by the technique of Page, et al [16-18]. Bond shear strength was then the ratio of the failure load to the bonded area.

The work discussed here is a continuation of that described above. Our main objective was to assess the effect of polymeric strength additives on bond strength. Because of their large size these materials are precluded from entering the cell walls. In the small amounts typically used (1-2% based on the pulp) they have a negligible effect on the tensile strength of the individual fibers [9,19]. Although the ability of such material to improve sheet strength is widely appreciated and used commercially, Russell, et al [9] found no increase in fiber-fiber bond strength when the fibers were treated with either a melamine-formaldehyde resin or a polyamide polyamine epichlorohydrin resin. In view of the theories of paper strength [1,2] we decided to look more closely at these interactions. In addition we re-examined the effect of springwood vs. summerwood and refining on bond strength.

EXPERIMENTAL

Materials

Small sections of earlywood and laterwood from loblolly pine were separately pulped using a conventional

kraft cook. Following pulping and washing, the sections were gently defibered and stored at low consistency [20].

For most of this work a conventional kraft cook of southern pine chips to a 47.5% yield (kappa number of 34.2) was used. The pulp was refined in a Valley beater to 570 and 345 mL CSF. Portions of the beaten pulps were classified in a Britt jar using a 65 mesh bronze wire to remove the fines. Distilled water was washed through the fibers until the filtrate was visually free of fines.

To study the effect of chemical additives on bond strength, we used either of the following combinations:

A/C - polyamidepolyamine epichlorohydrin (PAE-1% based on pulp) followed by carboxymethylcellulose (CMC-0.4%). Espy [21] has shown that this ratio of the two polymers provides maximum sheet strength. The two polymers are cationic and anionic, respectively, and were added to dilute suspensions of the fibers sequentially with adequate time for adsorption. Under these conditions virtually all of the polymers are adsorbed [22]. It has been shown [23,24] that covalent bonds (ester) can be formed between the azetidinium groups on the PAE and carboxyl groups on either the fiber surface or the CMC.

D/C - polydiallyldimethyl ammonium chloride (0.5%) followed by sodium polystyrene sulfonate (0.5%). These two are highly charged cationic and anionic polymers,

respectively, and are added to the fibers similarly to the A/C combination. Because of their chemical structure the only interactions possible are ionic: either between the cationic "D" and ionized carboxyl groups on the fiber surface or between "D" and the sulfonate groups on "S".

The pH of the fiber suspensions were near neutral, and no other additives were present.

Techniques

To obtain better contrast between bonded and unbonded areas determined using the vertical illumination, polarized light scattering method [16-18], we followed Page's technique [16] and dyed a separate portion of each set of fibers with Chlorazol Black E (before polymer treatment).

Fiber/fiber bonds were formed as follows. A dyed and an undyed fiber (each from a batch of strength aid-treated fibers, if desired) were positioned at right angles to each other on a teflon-faced silicone rubber disc (Microsep F-138, Supelco Inc) under water. A second disc was placed teflon face down on top of the fibers. The fiber pair was then dried in a oven at 105° C for one hour under a nominal compressive load of 0.12 MPa. The actual load in the fiber crossing (bonding) area would be

somewhat greater, but the softness of the teflon and rubber backing would tend to reduce the pressure.

After drying, the now-bonded fiber pair was placed on a Mylar mount (Fig. 1) with the dyed fiber next to the mount and coaxial with the "tongue". The mount was fabricated from 0.010" thick Mylar by laser machining. The solid line in Fig. 1a) is a 0.007" slot cut by the laser. The fibers were attached at both their ends to the mount with Epon 907 or a hot melt. (The drawing is to scale except the fibers have been shown at about five times their real width for clarity).

Both bond formation and bonded-fiber mounting were carried out under a binocular microscope.

The scattered light from the individual fiber/fiber bonds using Page's technique [16-18] was photographed. Slides (35mm) were prepared and projected. The bonded (dark) area was traced and its area determined using an Apple Graphics Tablet connected to an Apple II microcomputer. The system was calibrated using an area of known size to convert the (optically) bonded area to units of square micrometers.

After determination of the bonded area, the Mylar mount was installed in the clamps of the FLER2. The latter is a second generation fiber-load-elongation-recorder [25] with increased sensitivity and versatility [26]. The parts of the Mylar mount shown as dotted lines

in Fig. 1a were cut using a hot wire and the bond was strained to failure. The load at failure was recorded. Because the fibers are only attached to the mount at their ends, the region of the bond is free to rotate out of the plane, and the stress geometry is not pure shear but contains a peeling component. Observation of the bond with a binocular microscope during straining revealed only a catastrophic failure. Partial debonding for stresses lower than the ultimate did not occur.

The FLER 2 was located in a room with the atmosphere controlled at 23°C and 50% RH, and the tests were made at those conditions.

The two parts of the Mylar mount each with its fiber (Fig. 1b) were removed from the clamps of the FLER2, coated with gold-palladium *in vacuo*, and installed in a scanning electron microscope. Formerly bonded areas were easily recognized and the locus of failure could be seen [22]. Analysis of this information will be the subject of a separate publication.

RESULTS AND DISCUSSION

The mean values of the bond breaking load, bonded area, and their ratio (load/area), the bond strength, are given in Table I for the various samples. Between 40 and 50 bonds were tested for each sample and the standard

deviations of the three properties are given in parentheses in the table. The large standard deviations are likely a result of several factors: 1. The inherent variability of the fibers themselves [5]. Nordman and Qvickstrom [7] showed that the tensile breaking load of fibers taken from a narrow position within a growth ring exhibited low variability. The present fibers were either from throughout an earlywood or latewood region or were a mixture of early - and latewood. Thus fiber wall thickness and fiber flexibility varied from fiber to fiber. For the beaten pulp the effect of the refining probably varied along the length of a fiber as well as from fiber to fiber. 2. Morphological features (eg pits) will vary along a fiber and from fiber to fiber and will affect the intimacy of interfiber conformability and bonding. 3. The relative proportions of shear and peeling will vary from one bond to the next. A greater degree of peeling would be expected to lower the bond breaking load and the calculated bond strength.

TABLE I. Mean Fiber Bond Properties

Fiber	Additives[a)]	Load, grams	Area, microns^2	Bond Strength, N/mm^2
Earlywood	-	0.47 (0.48)[b)]	2410 (840)	2.1 (2.1)
Latewood	-	0.87 (0.56)	1500 (540)	6.4 (4.2)
Earlywood	A/C	1.14 (0.48)	3000 (770)	3.9 (1.7)
570 mL CSF	-	0.73 (0.65)	2070 (720)	3.5 (2.8)
345 mL CSF	-	0.68 (0.48)	2290 (1070)	3.7 (4.4)
570 mL CSF	A/C	1.44 (1.22)	2130 (800)	7.5 (6.7)
570 mL CSF	D/S	1.51 (0.92)	2040 (740)	9.3 (5.7)

a) Fibers treated with A/C (see text) or D/S polymers.
b) Values in parentheses are standard deviations

In spite of the large variability (and standard deviation), the results are amenable to interpretation. Comparisons between samples for a particular property were tested using the t-statistic. In the following discussion statements regarding either the inequality or the equality between two values can be made with a probability of their being valid of greater than 99%.

Representative results (probability plots) for breaking load, bonded area and bond strength are shown in Figs. 2-4 (for earlywood). Bond strength as noted previously [8] and load follow log normal while bonded area follows a normal distribution. The results for the other samples also clearly follow these same distributions, although the scatter in some cases is greater. In contrast, Mohlin [10] found a normal distribution for the bond strength of cellulose fibers bonded to cellophane.

It would be expected that there would be a linear relationship between the load and the bonded area. In reality there is not, and the only other comparable data given in detail in the literature [6] also fail to show the expected trend. Likely, this is a result of one (or more) of the three factors leading to variability discussed above.

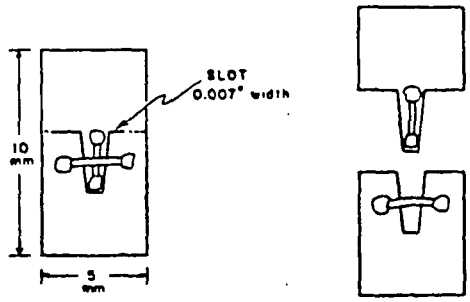

FIG. 1 MYLAR BONDED FIBER MOUNT. a) INTACT b) AFTER DIVIDING THE MOUNT AND STRADDLING THE BOND TO FAILURE

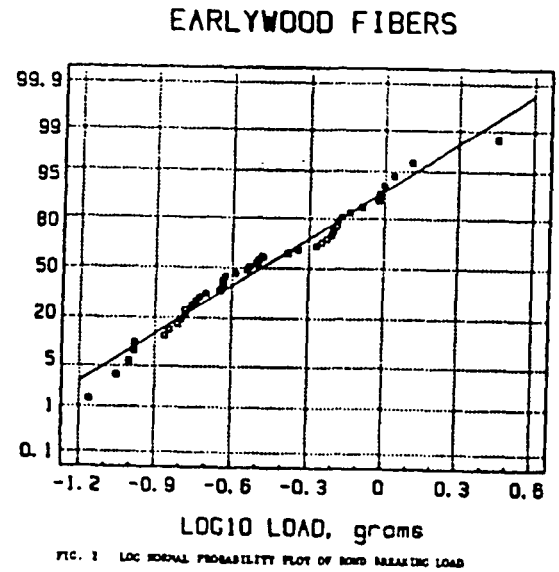

FIG. 2 LOG NORMAL PROBABILITY PLOT OF BOND BREAKING LOAD

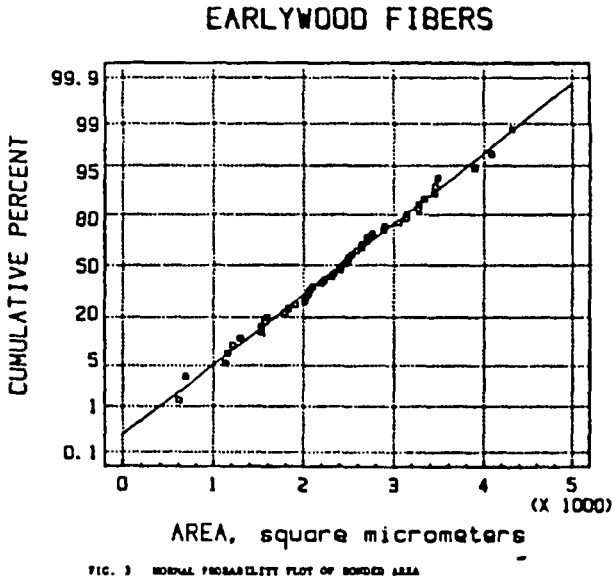

FIG. 3 NORMAL PROBABILITY PLOT OF BONDED AREA

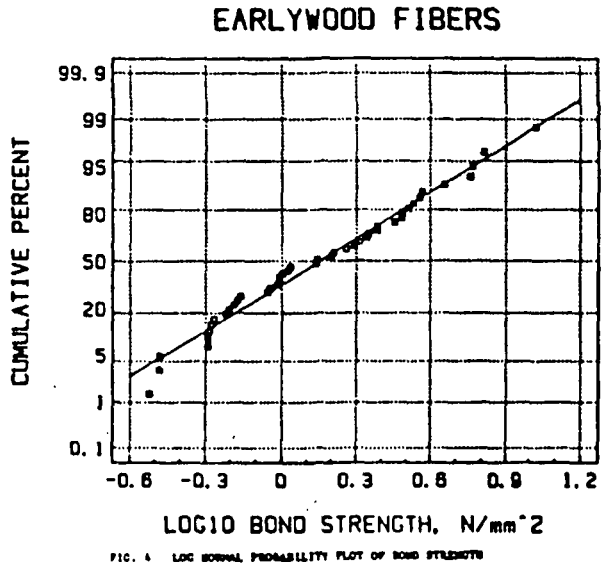

FIG. 4 LOG NORMAL PROBABILITY PLOT OF BOND STRENGTH

Earlywood vs Latewood

Several workers [7,8,15] have shown latewood fiber bonds to have a higher strength than earlywood bonds. Mohlin [10], on the other hand using fibers bonded to cellophane found no difference in strength between them

for four different pulps. The present results show that for both breaking load and bond strength the latewood fibers are stronger. As expected for the thicker-walled, less conformable latewood fibers, their bonded area is much smaller. Mohlin [10] argues that the bond strength is a function only of the surface chemistry of the fibers and therefore would be expected to be the same for early and latewood. Perhaps the difference between her work and that of the other workers and the present study lies in the experimental geometry. The stress distribution in the case of a fiber/fiber bond would be expected to be influenced more by cell wall thickness than would the fiber/cellophane bond. The fiber/fiber bond geometry may be closer to the situation prevailing in a sheet of paper.

Effect of Refining

In agreement with previous workers [6,12], we find no statistically significant difference between the properties of bonds between fibers from pulps refined to 570 and 345 mL CLS. It may be that already at 570 mL CSF most of the S1 layer has been removed, and bonding is primarily between the S2 layers of the two fibers, with

a similar situation at 345 mL CSF. It could be argued that unrefined fibers with S1 intact might have different bonding properties. We do not have such a comparable sample, unfortunately. On the other hand, the load and bond strength for the refined samples fall between those for the unrefined earlywood and latewood as might be expected since they comprise a random sample of refined early - and latewood fibers.

Effect of Strength Aids

When the earlywood fibers are treated with A/C all three bond properties increase. This disagrees with the results of Russell, et al [9] cited previously. The fact that a measurable increase in bonded area occurs may be attributed to the thin walls and great flexibility of earlywood fibers. Perhaps the strength aid is effective here in reducing "springback" during drying which tends to decrease the bonded area.

For the refined pulp both strength aid combinations (A/C and D/S) are equally effective in improving load and bond strength. As with the earlywood fibers greatly enhanced bond strengths are produced. Here (perhaps because the samples include both early - and latewood), no change in bonded area is found. The fact that A/C and

D/S produce comparable results is surprising. The former can interact with the cellulosic fibers via hydrogen, ionic, and covalent bonds whereas the latter has only the possibility of ionic bonds. Evidently, covalent bonds are not necessary for high strength. Although ionic bonds can provide only temporary wet strength, they have the advantage (over strength aids forming covalent bonds) of being readily repulpable. Such strength aids may find increased use in the near future in paper designed to be recycled. We have recently shown [28] that strength aids such as A/C and D/S can shift sheet strength from being bond strength limited to being fiber strength limited even with high yield pulps.

CONCLUSIONS

Latewood fibers produce stronger bonds than do earlywood fibers. Refining has negligible effect on bond strength. Polymeric strength aids interacting with the fibers by either covalent or ionic bonds can increase the fiber/fiber bond strength by a factor of two or more.

ACKNOWLEDGEMENT

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